# A complex study of vibrational spectra of natural analcime

F. PECHAR and D. RYKL

Institute of Geology and Geotechnics, Czechoslovak Academy of Sciences, CS-182 09 Prague

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The vibrational spectra of natural zeolite, *i.e.* analcime (locality Husa), in medium region of infrared radiation ( $\tilde{v} = 4000-200 \text{ cm}^{-1}$ ) and in far infrared region (f.i.r.) ( $\tilde{v} = 400-40 \text{ cm}^{-1}$ ), as well as the infrared reflection spectra ( $\tilde{v} = 1400-200 \text{ cm}^{-1}$ ) and the spectra of Raman scattering of a polycrystalline sample ( $\tilde{v} = 3600-50 \text{ cm}^{-1}$ ) were measured. By means of the program KKK-1, the dispersion curves of the complex index of refraction and of both parts of the complex dielectric permittivity were calculated from the reflection spectra. On the basis of experience and literature data, the spectral bands were assigned to the vibrations of individual bonds in the structure of analcime.

Были измерены колебательные спектры природного цеолита анальцима (местонахождение Гуса) в средней волновой области инфракрасного излучения ( $\tilde{v} = 4000-200 \text{ см}^{-1}$ ) и в удаленной инфракрасной области ( $\tilde{v} = 400-40 \text{ см}^{-1}$ ), инфракрасные отражательные спектры ( $\tilde{v} = 1400-200 \text{ см}^{-1}$ ), и спектры комбинационного рассеяния поликристаллического образца ( $\tilde{v} = 3600-50 \text{ см}^{-1}$ ). С помощью программы ККК-1 из отражательных спектров были рассчитаны дисперсионные кривые комплексного коэффициента преломления и обеих частей комплексной диэлектрической проницаемости. На основе опыта и литературных данных, касающихся подобных веществ, отдельные полосы спектра были приурочены колебаниям соответствующих связей в структуре анальцима.

There are three principal methods that can be used for measuring the vibrational spectra of crystals:

- 1. Measurement of absorption of infrared radiation,
- 2. measurement of reflectance of infrared radiation,
- 3. measurement of Raman scattering of visible radiation.

These methods complete each other not only from the view-point of experimental technique but also from the view-point of use of the selection rules [1]. The spectra obtained enable us to determine the wavenumbers and intensities of the bands of individual vibrations and to use them for calculating the dispersion of optical constants (index of refraction, dielectric permittivity, extinction), the force constants, and the dispersion of electric dipole moment. Furthermore, we may determine from the spectra the vibrations of individual bonds, their type and symmetry as well as the mean square amplitudes of vibrations and thus obtain complementary information about structure and dynamics of the crystal lattice. For this reason, the optical methods represent a necessary complement of the X-ray diffraction methods (or neutron diffraction methods) in a complex study of crystalline substances [1].

In this paper, we are not concerned with the theory of individual spectroscopic methods because it is presented in specialized studies and manuals of infrared and Raman spectroscopy [1-3]. The aim of this paper is to show by the example of natural zeolite — analcime in the first approximation the possibility of using the methods of vibrational spectroscopy for a complex study of crystalline (especially mineral) substances.

#### **Experimental**

The infrared absorption spectra of natural zeolite — analcime of ideal crystallochemical formula Na<sub>10</sub>(Al<sub>16</sub>Si<sub>32</sub>)O<sub>49</sub> · 16H<sub>2</sub>O (locality Husa) were measured in the wavenumber range 4000—200 cm<sup>-1</sup> [5] with a double-beam spectrometer Perkin—Elmer 325. The samples of analcime were prepared in the form of KBr tablets (mass ratio 1:40) and the spectra were taken at normal temperature and atmospheric pressure (Fig. 1). The infrared absorption spectra in far region (f.i.r.) occurring in the wavenumber range 400—40 cm<sup>-1</sup> were taken with an infrared interferometer Beckman FS-720 (Fig. 2). The samples were prepared in a polyethylene foil (mass ratio 1:20) at 200 °C and subjected to measurement *in vacuo* (oil vacuum pump) at normal temperature.



Fig. 1. Infrared absorption spectrum of analcime in the wavenumber range 4000-200 cm<sup>-1</sup>.



Fig. 2. Infrared absorption spectrum of analcime in far region in the wavenumber range  $400-40 \text{ cm}^{-1}$ .

The spectra were evaluated by the Fourier method with a computer (IBM 370).

The reflection spectra in infrared region were recorded at normal temperature and atmospheric pressure with a prism spectrometer Specord 75 (Zeiss, Jena) in the wavenumber range  $1400-400 \text{ cm}^{-1}$  (Fig. 3) and with a spectrometer Perkin—Elmer 325 in the wavenumber range  $400-200 \text{ cm}^{-1}$  (Fig. 3).

The samples used for measurement were prepared in the form of optical polished surfaces (prepared by P. Baxa, ÚVR Prague). The values of reflectance R/% read 5 cm<sup>-1</sup> by 5 cm<sup>-1</sup> and referred to an Al-mirror were processed by the program KKK-1 [6] and used for calculating the dispersion curves of the complex index of refraction and both components of



Fig. 3. Infrared reflection spectrum of analcime in the wavenumber range 1400-200 cm<sup>-1</sup>.

the complex dielectric permittivity (Figs. 4—6). The spectra of Raman scattering of a polycrystalline sample were recorded on a laser spectrometer SPEX 14018 ( $\lambda_{Ar}$  = 514.5 nm) at normal temperature and atmospheric pressure in the wavenumber range 3600—50 cm<sup>-1</sup> (Fig. 7). The samples were prepared for measurement by glueing the crystals on a quartz rod.



Fig. 4. Dispersion curve of the complex index of refraction of analcime calculated from i.r. reflection spectra by means of the program KKK-1.



Fig. 5. Dispersion curve in real region of the complex dielectric permittivity of analcime calculated from i.r. reflection spectra by means of the program KKK-1.



Fig. 6. Dispersion curve in imaginary region of the complex dielectric permittivity of analcime calculated from i.r. reflection spectra by means of the program KKK-1.



Fig. 7. Spectrum of Raman scattering of visible radiation of a polycrystalline sample of analcime in the wavenumber range 4000-50 cm<sup>-1</sup>.

The chemical quantitative analyses of the samples of analcime (locality Husa) gave results listed in Table 1. The evaluation of all vibrational spectra is presented in Table 2.

Oxide	w/mass %	
SiO <sub>2</sub>	61.38	
$Al_2O_3$	19.36	
CaO	0.23	
$P_2O_5$	0.00	
BaO	0.00	
Na <sub>2</sub> O	10.46	
K <sub>2</sub> O	0.21	
TiO <sub>2</sub>	0.01	
MgO	0.001	
$Fe_2O_3$	0.07	
MnO	0.00	
SrO	0.006	
H <sub>2</sub> O total	7.88	L-1 1 100-1
Altogether	99.61	

## Table 1

# Chemical composition of analcime (locality Husa)

## Table 2

Bond vibration	IR	FIR	Reflectance	Raman	
	√/cm <sup>-1</sup>				
Antisymmetric and symmetric O—H stretching	3610—3550 vs		_	3650 vw 3643 w 3600 vw	
Combined band of libration and bending vibration of H <sub>2</sub> O	2910 vw 2840 w	_	_	-	
Bending H—O—H	1630 m		-	—	
Antisymmetric T—O stretching	1000—1020 vs	-	_	1050 vw 1020 vw 940 w 880 s 810 s	
Symmetric T—O stretching	730 m 765 m		770 s 675 m	780 w 720 w 660 w	

### Evaluation of all investigated vibrational spectra of analcime

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VIBRATIONAL SPECTRA OF ANALCIME

Road vibration	IR	FIR	Reflectance	Raman		
	$\tilde{\nu}/\mathrm{cm}^{-1}$					
Bending	615 w	400 s	447 w	525 vw		
0—T—0	440 vs		425 vs	440 vs		
External		372 m	375	365 101		
between TO.	_	572 m	365 w	505 VW		
			346 w			
			330 m			
	210	205		210		
Translational mode of H O	310 w	305 vw		310 vw		
hibde of H <sub>2</sub> O						
Na—O	_	252 w	258 vw	270 vw		
		210 m		98 vw		
		198 w				
		98 w				
Na-H.O		160 w	_	160 m		
1120		110 w		100 11		
Translational	_	105 w	_	_		
mode of		86 w				
lattice		72 w				
		58 w				

Table 2 (Continued)

 $\Gamma_{vib} = 13A_{1g}(R) + 13A_{2g} + 26E_g(R) + 39F_{1g} + 13A_{1u} + 13A_{2u} + 26E_u + 39F_{1u} + 39F_{2u}(IR)$ vs — very strong, s — strong, m — medium, w — weak, vw — very weak.

#### Discussion

All investigated spectra give well distinguishable vibrational bands with relatively low background. The accuracy in reading the wavenumbers of individual bands varied for all bands in range  $\pm 2$ —5 cm<sup>-1</sup>. The wavenumbers were assigned to individual vibrations on the basis of experience and literature data [5, 7].

According to range of the measured wavenumbers, we may compare the investigated spectra with each other in three groups:

1.  $3700-1400 \text{ cm}^{-1}$  — infrared absorption spectra in medium region and spectra of Raman scattering,

2.  $1400-200 \text{ cm}^{-1}$  — infrared absorption spectra in medium region, a part of f.i.r. spectra, infrared reflection spectra, and Raman spectra,

3. 200-40 cm<sup>-1</sup> - f.i.r. spectra and Raman spectra.

1. The bands (antisymmetric and symmetric) of stretching vibration of the

hydroxyl groups appear in the wavenumber range  $3610-3550 \text{ cm}^{-1}$  in the infrared spectrum and exhibit high intensity. The bands of this vibration occur in the spectra of Raman scattering (R) in the wavenumber range  $3650-3600 \text{ cm}^{-1}$  and are weak. The bending H-O-H vibration has the wavenumber  $1630 \text{ cm}^{-1}$  in the i.r. spectrum and its maximum shows medium intensity. This band has not been found in the Raman spectrum [4].

2. In the infrared and Raman spectra we may observe the bands of antisymmetric stretching vibration with variable intensity of the tetrahedral T—O bonds in the wavenumber range  $1050-810 \text{ cm}^{-1}$ . These bands do not appear in the infrared reflection spectra. Except the f.i.r. spectra, we can identify in all investigated spectra the bands with medium or low intensity which may be attributed to symmetric stretching vibration of the T—O (T=Si, Al) bonds. These bands occur in the wavenumber range  $780-660 \text{ cm}^{-1}$ . The bending vibration of the tetrahedral bonds exhibits the bands in the wavenumber range  $615-400 \text{ cm}^{-1}$ . The external vibration of the bonds between tetrahedrons gives rise to the bands of different intensity in all investigated spectra which appear in the wavenumber range  $375-330 \text{ cm}^{-1}$ . In the wavenumber range  $310-305 \text{ cm}^{-1}$  of all investigated spectra (except the reflection spectra) the translational mode of the molecules of H<sub>2</sub>O is likely in interaction with the lattice of the crystal of analcime.

3. The bands of the translational mode of the Na—O bond which exhibit different intensities appear in the wavenumber range  $270-160 \text{ cm}^{-1}$ . The bands under the wavenumber of  $160 \text{ cm}^{-1}$  may be attributed to the vibration of a cation—water complex or translational mode of the crystal lattice of analcime.

The calculated dispersion curves of the complex index of refraction and of both components of dielectric permittivity exhibit a similar course of maxima like the reflectance of infrared radiation, which is in good agreement with the theory [1].

#### Conclusion

The study of complex vibrational spectra of crystalline substances gives a rapid information about the presence of vibrations of a certain symmetry in the structure of crystals, the dispersion of optical constants in the whole range of wavelength measurements, the presence of crystal water, and the structural hydroxyl groups and thus it is a necessary complement of the X-ray diffraction methods which are more and more used in technological practice.

The infrared spectra in medium region are especially suited to determination of the character of the bonds of water molecules (presence of hydrogen bonds, *etc.*). The spectra in far infrared region are suited to determination of the character of the bonds of the cations and their complexes in the holes of zeolites. The infrared reflection spectra give outstanding maxima due to vibrations of the tetrahedral bonds and lattice modes. The spectra of Raman scattering cover the whole range of vibrations but they are less sensitive to the vibrations of water molecules and hydroxyl groups.

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